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Laboratory Spectroscopy of CH^+ and isotopic CH

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ABSTRACT

The $A^1\Pi - X^1\Sigma$ electronic band of the CH^+ ion has been used as a probe of the physical and dynamical conditions of the ISM for 65 years. In spite of being one of the first molecular species observed in the ISM and the very large number of subsequent observations with large derived column densities, the pure rotational spectra of CH^+ has remained elusive in both the laboratory and in the ISM as well. We report the first laboratory measurement of the pure rotation of the CH^+ ion and discuss the detection of $^{13}\text{CH}^+$ in the ISM. Also reported are the somewhat unexpected chemical conditions that resulted in laboratory production.

1. Introduction

The $A^1\Pi - X^1\Sigma^+$ system of CH^+ was first observed by Douglas & Herzberg (1941) and later the 0-0 1-0 and 2-0 vibrational sub-bands were analyzed (Douglas & Herzberg 1942). The laboratory spectrum confirmed CH^+ as a major constituent in interstellar clouds (Adams 1942). In spite of the astronomical significance, subsequent laboratory work on CH^+ has been relatively limited. The original data was extended to include the 0-1, 1-1, 2-1, 3-1 and 4-1 bands and Douglas & Morton (1960) extended the previous analysis to include the 0-1, 1-1, 2-1, 3-1 and 4-1 vibrational sub-bands. Later the 3-0 and 4-0 vibrational sub-bands of the $A^1\Pi - X^1\Sigma^+$ system and the $^1\Delta - ^1\Pi$ system and the $^3\Sigma - ^3\Pi$ systems were observed by Carre (1968). The 0-0, 0-1, 1-0, 1-1, 1-2, 1-3, 2-1 and 3-1 vibrational bands of the $A^1\Pi - X^1\Sigma^+$ system were remeasured at higher resolution and a complete set of molecular constants for the ground state of CH^+ were determined (Carrington & Ramsay 1981).

Laboratory investigations of isotopic CH^+ have been similarly limited with all the available data coming from the electronic bands. The $A^1\Pi - X^1\Sigma^+$ system was first tentatively identified on the basis of interstellar spectra (Bortolot & Thaddeus 1969), which led to a

laboratory investigation of the 0-0, 1-0, 1-0, 2-1, 2-0 and 3-1 vibrational sub-bands (Antić-Jovanović et al. 1983) confirming the identification. The spectrum of $^{13}\text{CH}^+$ in the 0-0, 0-1, 1-0, 1-1, 2-0 and 2-1 bands $A^1\Pi - X^1\Sigma^+$ system was revisited and recorded to higher J values (Bembenek 1997a). The $A^1\Pi - X^1\Sigma^+$ system of CD^+ was first observed by Cisak & Rytel (1971). The initial study was extended to the 0-0, 1-0, 2-0, 0-1, 2-1 and 3-1 vibrational sub-bands (Antić-Jovanović et al. 1979). The 0-0 and 2-1 bands of CD^+ were also measured by Grieman et al. (1981). The most complete analysis of the $A^1\Pi - X^1\Sigma^+$ system of CD^+ including the 0-0, 1-0, 2-0, 0-1, 2-1, 3-1, 1-2 and 1-3 vibrational sub-bands was reported by Bembenek et al. (1987). There is only one reported investigation of the $A^1\Pi - X^1\Sigma^+$ system in $^{13}\text{CD}^+$ where the 0-0 and 1-0 vibrational sub-bands were recorded (Bembenek 1997b).

Reconciling the observed CH^+ abundance in the interstellar medium with a chemical production mechanism has been a long standing problem (e.g. Bates & Spitzer (1951); Black & Dalgarno (1973); Black et al. (1975); Black (1998)). CH^+ requires H_2 for formation, but is quickly destroyed by H_2 as well. Radiative association of C^+ with H_2 is too slow to account for the destruction (Black et al. 1978) and the direct formation is endothermic and therefore inconsistent with the cold gas optical line widths (Crane et al. 1995; Gredel 1997). Heterodyne observations would clearly determine the origin of the CH^+ in the interstellar medium and would constrain the variety of mechanisms invoked to produce the large observed column densities.

The $J = 1 - 0$ transition of CH^+ is unfortunately close to the $J = 5 - 3$ Oxygen line at 834.1 GHz. As a result, it cannot be directly observed from the ground and the only astronomical detection was from ISO at too low spectral resolution to address the chemical origins questions (Cernicharo et al. 1997). However, the $^{13}\text{CH}^+$ $J = 1 - 0$ transition is shifted far enough away from the oxygen line to facilitate detection.

2. Astronomical Detection of $^{13}\text{CH}^+$

A search for $^{13}\text{CH}^+$ based on the optical constants was carried out from the Caltech Submillimeter Observatory towards the bright star forming region G10.6-0.4. Two features were subsequently detected one in emission and one in absorption. In this source there are three gas phase components along the line of sight. The Star forming region G10.6-0.4, an extended CO emission region and a deep HI self absorption region without CO have velocities (v_{LSR}) of -2 km/s, +29 km/s and +7 km/s, respectively. The emission line was assigned to A state methanol $7_2^+ - 6_1^+$ in the star forming region. However, the candidate $^{13}\text{CH}^+$ line could have a frequency of 830107, 830193 or 830132 MHz depending on the component of the ISM where it originated (Falgarone et al. 2005). An analysis of the $^{13}\text{CH}^+$ optical spectrum (Bembenek 1997a) resulted in a predicted frequency of 830150 GHz but the error bars did not preclude any of the possibilities.

3. Laboratory detection of CH⁺

Laboratory studies of CH⁺ have been problematic due to uncertainty in the chemical production mechanism and technical challenges in generating microwaves at 835 GHz. The microwave challenge was addressed by constructing a new direct synthesis spectrometer (Drouin et al. 2005). Next, a new magnetically enhanced (De Lucia et al. 1983), variable temperature discharge cell was constructed. As a commissioning experiment four transitions of HCO⁺ in the ground and first excited vibrational were observed between 800 and 900 GHz. This data is listed on Table 1 and compared to the frequencies in the JPL and CDMS line catalogs. We had previously believed that HCO⁺ was sufficiently well studied for Herschel, SOFIA and ALMA, but this is clearly not the case and it will be the subject of a separate investigation.

Table 1: HCO⁺ transitions from this study, catalog entries and other experiments.

Ju-Jl	V	Measured	JPL Catalog	Cologne Database
9-8	0	802458.217(50)	802458.329(400) ^a	802457.970(133) ^b
10-9	0	891557.340(50)	891557.924(272) ^b	891557.038(203) ^b
9-8	1	802039.104(75)	802939.079(400) ^c	802038.613(413) ^b
9-8	1	805845.625(75)	805845.788(400) ^c	805845.545(464) ^b

^avan den Heuvel & Dymanus (1982)

^bCalculated

^cBlake et al. (1987)

The initial series CH⁺ experiment started with acetylene and argon, but the only line detected was from CH₃CCH. A second series of experiment with improved cell cooling and helium and argon was carried out. CH⁺ was discovered at 835078.950(75) GHz in a clean cold cell with slow pumping speed at the start of the experiment. If the cell warmed up, the 12_{0,12} – 11_{0,11} line of H₂¹³CO would appear at 835085.16 GHz and the CH⁺ line would disappear. The axial magnetic field and some helium were required for CH⁺ production. Additionally the CH⁺ signal degraded as the experiment ran and coated the walls with hydrocarbons. CH⁺ was also produced in a methane discharge under similar conditions but at a lower methane flow rate since methane does not freeze out at the 90K cell wall temperature. The best signal-to-noise always came from the highest voltage discharge that was stable.

4. The Astronomical Origins of ¹³CH⁺

In order to determine the origin of the ¹³CH⁺ line two analyses of the new laboratory frequency were carried out. First, the data from Carrington & Ramsay (1981) and Cernicharo et al. (1997) were combined with the new laboratory frequency and a complete set of Dunham constants (Dunham 1932) determined for CH⁺. Table 2 gives the constants for

CH⁺ determined from this analysis. The 3-1 band was excluded from the analysis since it shows systematic deviations consistent with a perturbation of the upper state. The analysis improved by a tiny amount when the laboratory frequency was included. From these parameters for ¹³CH⁺ were derived using isotopic ratios. This resulted in a 830131.4(2.4) MHz frequency without accounting for Born-Oppenheimer breakdown (Watson 1973). A second analysis was performed by fitting all the isotopic data including the Born-Oppenheimer breakdown terms. This resulted in a 830166 MHz frequency with a large uncertainty. The magnitude of the Born-Oppenheimer breakdown correction is known for CO (Wappelhorst et al. 1997) and equates to +1.5 MHz. The correction from CH (Davidson et al. 2004) was estimated on the basis of the B constant, which does not properly account for the vibrational dependence and therefore over estimates the correction at +20 MHz. This leads to the conclusion that the correction is small and positive. The only viable candidate from the ISM is deep HI component without CO where the rest frequency is 830132(3) MHz.

Table 2: Derived Dunham constants for ¹²CH⁺.

Parameter	Value (MHz)
Y ₁₀ /2	42833117.(83)
Y ₂₀ /4	-444387.7(244)
Y ₃₀ /8	829.43(204)
Y ₀₁	425007.05(79)
Y ₀₂	-41.3855(250)
Y ₀₃ x10 ³	1.923(215)
Y ₁₁ /2	-7402.04(88)
Y ₁₂ /2	0.3426(38)
Y ₂₁ /4	16.544(93)
<i>n_{lines}</i>	211
<i>σ_{red}</i>	1.518
<i>σ_{red}</i> ^a	1.521

^a*σ_{red}* without the laboratory line.

5. Conclusions

The rotational spectrum of CH⁺ has been observed for the first time in the laboratory facilitating heterodyne astronomical observations from Herschel to constrain the chemical origins of CH⁺. The ¹³CH⁺ frequency and observation should facilitate follow up work along more lines of sight to confirm ¹³CH⁺ in the diffuse ISM and illuminate the non thermal component that leads to its production. The very large A coefficient of CH⁺ 5.9 x 10⁻³s⁻¹ should make it a major factor in the energy balance of the diffuse ISM providing an interesting window into this still poorly understood gas phase.

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